

Oxidation of A Low Carbon Steel in the Temperature Range 1650 to 2100 Degrees Fahr.

***By* Clarence A. Siebert and Clair Upthegrove**



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OXIDATION OF A LOW CARBON STEEL IN THE TEMPERATURE RANGE 1650 TO 2100 DEGREES FAHR.

BY CLARENCE A. SIEBERT AND CLAIR UPTHEGROVE

Abstract

A paper presented at the 14th annual convention of the American Society for Steel Treating by Upthegrove and Murphy (1) gave data on the scaling of S.A.E. 1020 steel in atmospheres of air, oxygen, steam, and carbon dioxide. They reported unexpected deviations in the temperature curves for both oxygen and air between 1800 and 2000 degrees Fahr., and pointed out that these deviations were accompanied by the formation of blisters on the surface of the steel. The present research was undertaken to further investigate these phenomena by a study of the effect of temperature, time, and partial pressure of oxygen in the scaling atmosphere in the temperature region 1650 to 2100 degrees Fahr.

LITERATURE

PREVIOUS researches on the general subject of scaling have been reviewed in previous publications from this laboratory by Murphy, Wood and Jominy (2)* and Upthegrove and Murphy (3). A brief survey of those publications which have a direct bearing on this investigation will be given here.

A large number of empirical researches giving actual scaling data have been reported. For the most part the investigators have used gain in weight as the criterion of scaling, a condition which does not always permit ready comparisons with the data obtained in this investigation in that the scaling was determined as loss in weight. Other than from the standpoint of the differences in the criterion of scaling, practically none of these researches have a direct bearing on the present study, since the temperatures used do not cover both the zones of increasing and decreasing scaling effects

*The figures appearing in parentheses refer to the bibliography appended to this paper.

Of the authors, Clarence A. Siebert is associated with the Metal Products Division, U. S. Rubber Co., Detroit, and Clair Upthegrove is Professor of Metallurgical Engineering, University of Michigan, Ann Arbor, Mich. Manuscript received June 20, 1934.

observed by Upthegrove and Murphy, or different atmospheres were used. Schroeder (4) using loss in weight as the measure of scaling reports an increase in scaling in combustion atmospheres on increasing the temperature from 1650 to 2190 degrees Fahr. (900 to 1200 degrees Cent.) as do Upthegrove and Murphy from 1500 to 1900 degrees Fahr. (815 to 1040 degrees Cent.). This, however, would be expected from the behavior of carbon dioxide and water vapor curves reported by Upthegrove and Murphy (5).

Heindlhofer and Larsen (6) derived an expression for the effect of time on scaling by means of differential equations and arrived at the conclusion that the oxidation was proportional to the square root of the time. They assumed a constancy of membrane structure which was not confirmed in the present investigation. They, however, investigated scaling over comparatively long periods of time. Their experimental data at 1020, 1110, 1830, 2010 degrees Fahr. (550, 600, 1000 and 1100 degrees Cent.) deviated considerably from the theoretical equation. They postulated that the interface of the various layers was composed of the mixed phases, that is $\text{FeO} + \text{Fe}_3\text{O}_4$, or $\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3$, and that the layers themselves were composed of the single solid solution beginning with Fe_2O_3 in the outer layer, Fe_3O_4 in the middle layer, and FeO in the inner layer. Their photomicrographs presented do not appear to offer confirmation of this statement.

Several theories have been advanced to account for the mechanism of oxidation. Pilling and Bedworth (7) suggested that the continued oxidation of a metallic surface occurred by reason of the diffusion of oxygen inward through the previously formed layers of scale. The scale had to expand outward because of the greater volume of the oxide compared with that of the metal. This necessarily assumes plastic properties for the scale, an assumption which, however, has been a point of serious objection.

Fedotjev and Petrenka (8) advanced the theory that the alternate formation and reduction of higher and lower oxides of iron were responsible for continued oxidation. In their mechanism they considered that FeO was formed first and then oxidized to Fe_3O_4 . The Fe_3O_4 was then reduced by the iron in contact with it to FeO so that additional iron was oxidized in this process. The FeO was oxidized again to Fe_3O_4 and the process repeated.

Pfeil (9) proposed a mechanism involving a double diffusional process, that is, the diffusion of oxygen inward accompanied by an

outward diffusion of some form of iron. This does not require the scale to have extreme plastic properties. In his investigations he has shown that scales of different iron contents can react with one another, that is when two samples of scale whose average iron contents were in excess of 72 per cent were heated in a vacuum or in purified nitrogen, an exchange of oxygen occurred until both samples had the same analysis. Likewise when a large amount of oxygen-rich scale was used so that the average iron content was less than 72 per cent, the iron-rich scale decreased in iron content to 72 per cent when the reaction stopped. Raising the temperature had no effect on changing the compositions of the two scales.

METHOD

The method used in this investigation was essentially the same as used by Upthegrove and Murphy (10). The samples were heated in an electric furnace of the Globar type which contained a glazed porcelain tube 40 inches long and approximately two inches in diameter. One end of the tube was sealed with a two-hole refractory stopper through which the gas inlet tube and thermocouple protection tube was led. In order to avoid scaling during the introduction of the sample into the furnace or during the time required for stabilizing the furnace temperature, the furnace was first thoroughly flushed with purified nitrogen. The flow of nitrogen was then continued while the sample was being introduced and the furnace brought to the predetermined temperature. The nitrogen was then cut off and the scaling agent turned on. At the end of the scaling period the oxidizing agent was cut off and the flow of purified nitrogen again turned on. The sample was immediately withdrawn and quenched in distilled water. The sample was suspended in a chromel wire boat during the run and was placed so that it was centered in the furnace one quarter of an inch below the thermocouple bead.

The atmospheres used in the studies were mixtures of oxygen and nitrogen in varying ratios. The total volume of the gas was such that a linear velocity of thirty feet per minute was maintained. The atmospheres were obtained by adding oxygen or nitrogen to dry air, depending upon whether greater or smaller percentages of oxygen than that in the air were desired. All gases were carefully purified by passing them through trains consisting of calcium chloride, ascarite, and dehydrite tubes to affect removal of CO_2 and water

vapor. The flow was measured by means of flow meters of the friction type which were calibrated against a Sargent wet test meter. Gas analysis was used as a check on the computed percentages from the flow meter readings.

While the greater part of the scale always split off in the quenching operation, the small amount adhering was removed in an electrolytic stripping bath. The sample was then washed, dried, and weighed. The loss in weight was expressed in terms of pounds per 100 square inches of original surface. The scale that split off was filtered, dried, and analysed for ferrous and total iron.

The samples used were $2\frac{1}{2}$ inches long and $\frac{5}{8}$ inch in diameter, after machining and polishing through 00 emery paper. The analysis of the steel used was:

Carbon	0.20 Per Cent
Manganese	0.45
Silicon	0.17
Sulphur	0.030
Phosphorus	0.017

RESULTS

The scope of this investigation was limited to the influence of temperature, time, and partial pressure of oxygen in the oxidizing gas. The effect of the variation of gas velocity was not studied, for increasing the flow above five feet per minute does not affect the scaling loss.

Effect of Variation of Temperature

The data which were obtained when the temperature of exposure was varied from 1650 to 2100 degrees Fahr. (900 to 1150 degrees Cent.), using air and oxygen as the scaling media, are summarized in Fig. 1. Both curves show regions where the amount of scaling is actually lowered by increasing the temperature, the effect being more pronounced when air is used as the oxidizing medium than when oxygen is used. In air the scaling loss reaches a maximum at 1850 degrees Fahr. (1010 degrees Cent.) and a minimum at 2000 degrees Fahr. (1095 degrees Cent.), while in oxygen a maximum is reached at 1900 degrees Fahr. (1040 degrees Cent.) and a minimum at 1950 degrees Fahr. (1065 degrees Cent.). The chemical composition of the scales formed shows a similar trend in ferrous iron content. This is indicated in Fig. 2, where ferrous iron is plotted against temperature. A maximum ferrous iron content occurs

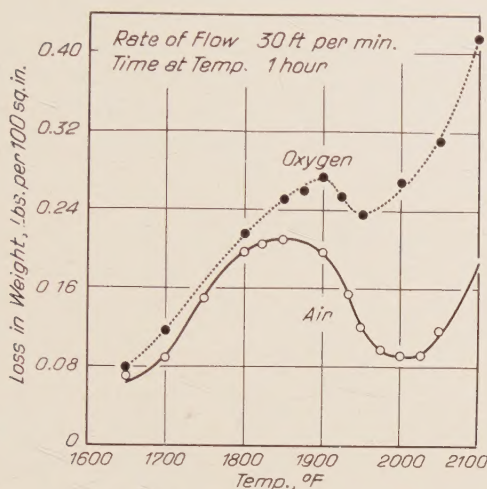


Fig. 1—Effect of Variation of Temperature on the Scaling of S.A.E. 1020 Steel.

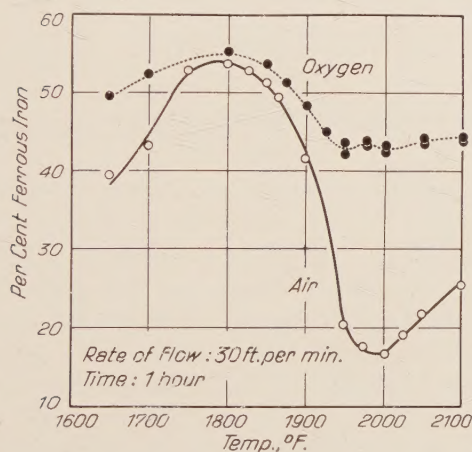


Fig. 2—Effect of Variation of Temperature on the Composition of the Scale.

at 1775 degrees Fahr. (970 degrees Cent.) and minimum at 2000 degrees Fahr. (1095 degrees Cent.) when air is the oxidizing agent. For the scale formed in oxygen, maxima occur at 1800 and 1975 degrees Fahr. (980 and 1080 degrees Cent.) and minima at 1950 and 2000 degrees Fahr. (1065 and 1095 degrees Cent.).

These data obtained by Upthegrove and Murphy (11) are sum-

marized in Fig. 3. A comparison of their results with those obtained in the present investigation shows certain differences to exist. They found in two hour scaling periods that the maximum scaling loss in air was reached rather abruptly at 1800 degrees Fahr. (980 degrees Cent.) and had fallen off considerably at 1900 degrees Fahr.

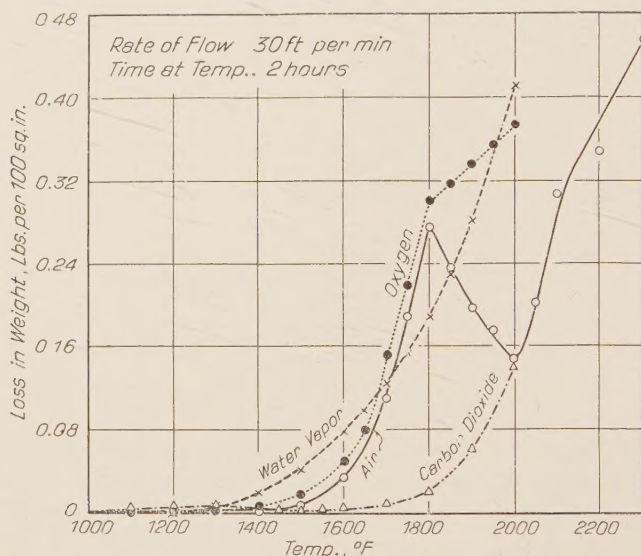


Fig. 3—Effect of Variation of Temperature on Scaling of S.A.E. 1015 Steel.

(1040 degrees Cent.). The present investigation, using a 1-hour period, shows the maximum to occur at 1850 degrees Fahr. (1010 degrees Cent.), with equal losses in weight at 1800 and 1900 degrees Fahr. (980 and 1040 degrees Cent.). Their work showed a retardation in oxygen at 1800 degrees Fahr. (980 degrees Cent.) while the present work not only shows a retardation at 1800 degrees Fahr. (980 degrees Cent.) or slightly above, but actually has a reversal at 1900 degrees Fahr. (1040 degrees Cent.). While at first it might appear that the differences were due to the use of different periods of scaling, the results of 2-hour tests in the present investigation, as shown in Fig. 4, clearly indicate this not to be the case. Chemical compositions of the steel do not offer an explanation in that the two are for all practical purposes identical.

	C	Si	Mn	P	S	H ₂	O ₂	N ₂
U-M	0.18-0.20	0.17-0.22	0.45-0.48	0.021	0.03	0.00004	0.005	0.005
S-U	0.20	0.17	0.45	0.017	0.03	0.00002	0.004	0.004

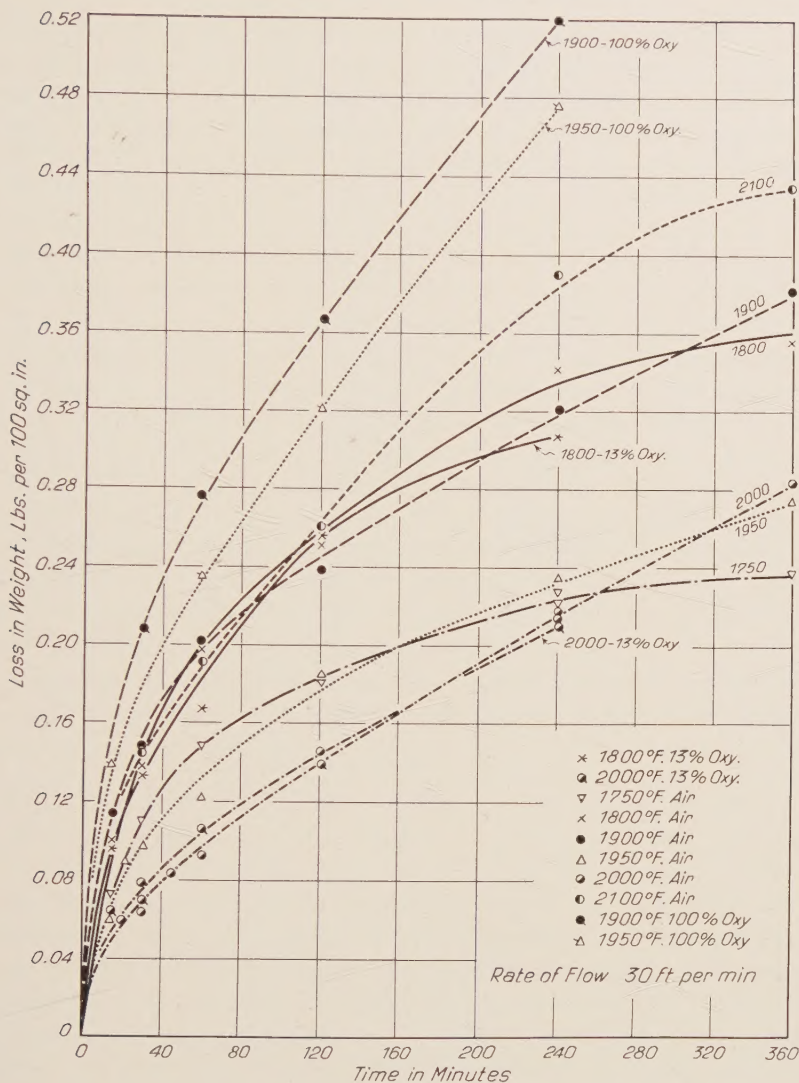


Fig. 4—Effect of Variation of Time on the Scaling Loss of S.A.E. 1020 Steel.

A difference, however, does exist in the method of production of the two steels. While both are open-hearth heats, the second was rolled from a small size ingot. It is known that differences in ingot size produce differences in physical properties and while this seems hardly probable it is possible that this may be a factor in the devia-

tions observed. The failure of Upthegrove and Murphy to report a reduction in scaling with increasing temperature in the oxygen atmosphere is more likely due to the fact that they used 50-degree temperature intervals rather than 25 degrees and as a consequence failed to observe definite indications of its occurrence. Their 1850 degrees Fahr. (1010 degrees Cent.) point actually fell slightly below the line joining the 1800 and 1850 degrees Fahr. (980 and 1010 degrees Cent.) points, but it was not looked on as significant at that time. As this stock was completely used up in the earlier investigation it was not possible to check this point.

Upthegrove and Murphy pointed out that the sudden change in the curves at 1800 degrees Fahr. (980 degrees Cent.) was accompanied by the formation of blister on the surface of the steel. They concluded that the blisters were areas where a higher degree of oxidation had occurred and due to the differences in specific volume of the different oxides of iron these blistered regions had buckled away, thereby interrupting the diffusional nature of the scaling process at these places. They believed that in time, contact would again be made, but in the meantime, the surrounding areas would have scaled to a greater extent, thereby creating the base relief pattern of the blisters. This will again be considered along with the authors' idea of the mechanism of this phenomenon.

Effect of Variation in Time

The effect of increasing periods of time on the oxidation of steel has been previously shown to produce data which when plotted result in curves of the parabolic type due to the diffusional nature of the scaling process. In the temperature range where blistering occurs it would then be expected that the data would plot as a broken curve if a mechanical interruption of the diffusional process occurred. If no mechanical effect existed a smooth curve of the parabolic type would be expected.

To determine whether or not such deviations would occur, time curves were obtained for oxygen, air, and 13 per cent oxygen at temperatures where scaling continued to increase with increasing temperatures and at temperatures where a decrease in scaling occurred with increasing temperatures. The effect of increasing periods of time on the scaling under these conditions is summarized in Fig. 4. In all cases, the effect of increasing time has been to decrease the rate of scaling and all curves are of the parabolic type.

The results obtained in oxygen at 1900 and 1950 degrees Fahr. (1040 and 1065 degrees Cent.) for periods of time up to four hours show that within the limit of time used there is no tendency for the rates of scaling to approach each other. Instead the decrease in the amount of scaling actually increases with increasing time. The increase in scaling losses in oxygen over those occurring in air also become greater at these temperatures as the time of contact is increased.

The study of the effect of time on the oxidation in air was carried out to six hours. Up to periods of four hours the curves rise rather rapidly with increasing time. Between four and six hours, however, the curves for 1750 and 1800 degrees Fahr. (955 and 980 degrees Cent.) tend to level off, while the curves for higher temperatures continue to rise at a practically unchanged rate with increasing time. A comparison of the scaling losses at the end of six hours with those at the end of one hour (Fig. 1) shows some changes in the form of the reversal. At the end of one hour at 1800 and 1900 degrees Fahr. (980 and 1040 degrees Cent.) equal losses in weight occur, and at 1950 degrees Fahr. (1065 degrees Cent.) a higher loss is found than at 2000 degrees Fahr. (1095 degrees Cent.). At the end of six hours, however, the loss at 1900 degrees Fahr. (1040 degrees Cent.) is slightly greater than at 1800 degrees Fahr. (980 degrees Cent.), and at 2000 degrees Fahr. (1095 degrees Cent.) exceeds that at 1950 degrees Fahr. (1065 degrees Cent.). Scaling loss at the end of one hour at 1800 degrees Fahr. (980 degrees Cent.) is greater than at 2100 degrees Fahr. (1150 degrees Cent.). The retardation effect with increasing time is greater at 1800 than at 2100 degrees Fahr. (980-1150 degrees Cent.) with the result that at the end of two hours the scaling is slightly greater at the upper temperature. This result is in agreement with the two-hour runs of Upthegrove and Murphy. Further increase of time up to six hours produces similar results with the rate of scaling at 2100 degrees Fahr. (1150 degrees Cent.) continuing to increase over that at 1800 degrees Fahr. (980 degrees Cent.).

The results obtained by scaling in an atmosphere containing 13 per cent oxygen at 1800 and 2000 degrees Fahr. (980 and 1095 degrees Cent.) show that the rates of scaling for periods up to two hours are slightly greater than in air at these temperatures. As the time is increased the retardation effect becomes more pronounced for the 13 per cent oxygen than for air, and the rate of scaling at

both 1800 and 2000 degrees Fahr. (980 and 1095 degrees Cent.) falls below that for air.

In interpreting the results of the time studies the question of whether or not the data point to the elimination of the reversal in the scaling or to its continuance with increasing periods of time occurs. While some of the above results seem to point very definitely

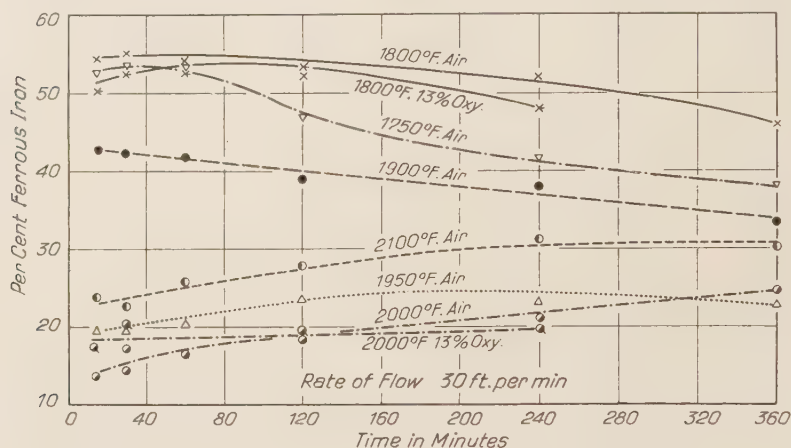


Fig. 5—Effect of Time on the Composition of the Scale.

to a smoothing out of the temperature effects, others indicate very definitely that this cannot happen unless the time is extended well beyond any of the heating periods employed in practice and possibly not then.

The scale analyses on the time runs are summarized in Fig. 5, where ferrous iron is plotted against time. For temperatures below 1950 degrees Fahr. (1065 degrees Cent.) the ferrous iron content decreases with increasing time, and above 1950 degrees Fahr. (1065 degrees Cent.) the ferrous iron content increases with increasing time. At 1950 degrees Fahr. (1065 degrees Cent.) the ferrous iron content reaches a maximum at three hours.

A study of the surface of the scaled samples appears to offer a partial explanation for these effects. Specimens that were scaled for different periods of time in air at 1950 degrees Fahr. (1065 degrees Cent.) are shown in Fig. 6. The roughening of the surface, which is related to the occurrence of blistering, makes its appearance almost instantly, in fact is unmistakable on samples subjected to the scaling medium for only five minutes. This roughening which is very ap-

parent in the 15 minute samples of Fig. 6 increases with increasing time and at the end of six hours the entire surface has been affected. The progressive effect with increasing time is found at all of the temperatures studied, and can account for the falling off in the ferrous iron content with increasing time at 1750, 1800 and 1900 degrees Fahr. (955, 980 and 1040 degrees Cent.), as the blistering



Fig. 6—Roughening of Surface of Sample Scaled in Air at 1950 Degrees Fahr. for Periods of Time Varying from 15 Minutes to 6 Hours.

is accompanied by the higher degree of oxidation. It does not explain, however, the rise in ferrous iron content with increasing time at 2000 and 2100 degrees Fahr. (1095 and 1150 degrees Cent.). The possibility that at these upper temperatures all layers of the scale do not grow proportionately appears to offer a feasible explanation. If it can be assumed that the inside layer grew faster than the outer layers, then the ferrous iron content of the scale would increase with increasing time. While not enough data are available to draw any definite conclusions in regard to this point, the suggestion of nonproportional growth of the different layers is not believed to be incompatible with observed facts.

Effect of Variation of Partial Pressure of Oxygen

The atmospheres for this phase of the investigation were obtained by adding carefully purified and dried oxygen or nitrogen to purified and dried air. The data obtained are summarized in Fig. 7. The curves divide themselves into two distinct groups; those which show a rapid rise in scaling with oxygen contents ranging from zero to approximately that of air, with a slight but gradual increase from

that point out to 100 per cent oxygen; and those which show a rapid rise in scaling at very low oxygen contents, and then a more gradual but greater increase from that point to 100 per cent oxygen.

The temperatures that produce curves falling in the first group are 1650 through 1900 degrees Fahr. (900 through 1040 degrees Cent.). Those producing curves falling in the second group are

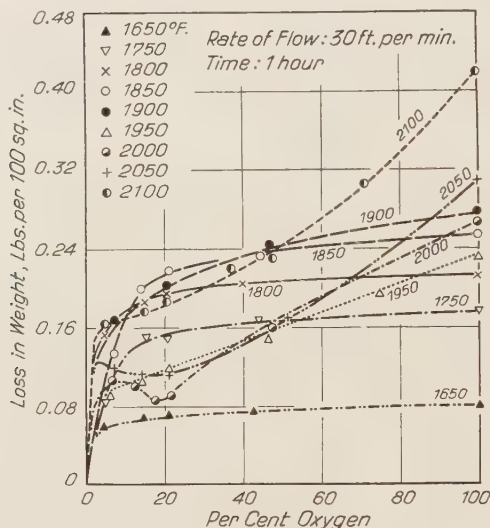


Fig. 7—Effect of Variation of Partial Pressure of Oxygen on the Scaling of S.A.E. 1020 Steel.

1950 through 2100 degrees Fahr. (1065 through 1150 degrees Cent.). Two other definite characteristics are evident in the graphs of the second group. The curvature of the 2050 and 2100 degrees Fahr. (1120 and 1150 degrees Cent.) curves is concave upward while all of the others have curvatures that are concave downward, with the exception of the 1950 degrees Fahr. (1065 degrees Cent.) curve which is a straight line between 4 and 100 per cent oxygen. The 2000 and 2050 degrees Fahr. (1095 and 1120 degrees Cent.) curves reach a maximum at 7 and 3 per cent oxygen respectively and minima at 18 per cent oxygen in both cases.

A comparison of the loss in weight values for the different temperatures and different oxygen concentrations with the chemical compositions of the scales formed, which are shown in Fig. 8, shows that the ferrous iron contents of the scales follow the same trend

as the loss in weight. The curves divide again into two groups; 1650 through 1900 degrees Fahr. (900 through 1040 degrees Cent.) and 1950 through 2100 degrees Fahr. (1065 through 1150 degrees Cent.). For temperatures of 1650 through 1950 degrees Fahr. (900 through 1065 degrees Cent.) the ferrous iron contents of the scales formed are nearly constant for oxygen concentrations of 20 to 100

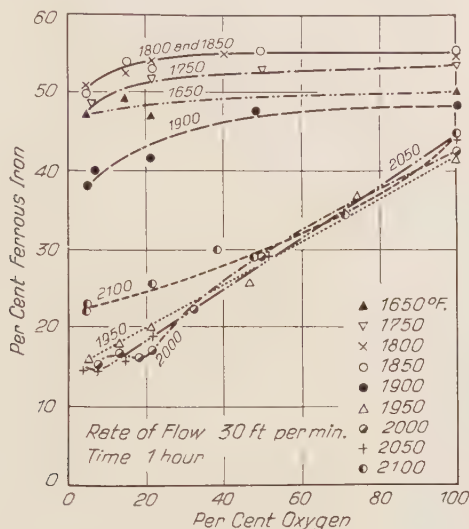


Fig. 8—Effect of Variation of Partial Pressure of Oxygen on the Composition of the Scale.

per cent. For temperatures of 1950 through 2100 degrees Fahr. (1065 through 1150 degrees Cent.) a very definite and fairly uniform increase in ferrous iron occurs with increasing oxygen concentrations.

Attention is also called to the evidence in these curves of the possibility of retarded scaling effects with increasing temperatures without the occurrence of a higher degree of oxidation. The losses in weight in a 40 per cent oxygen atmosphere at temperatures of 1950, 2000 and 2050 degrees Fahr. (1065, 1095 and 1120 degrees Cent.) are found to be approximately equal. Reference to Fig. 7 shows that the ferrous iron contents of the three scales are approximately identical. This is a departure from the effect usually obtained where the retardation is accompanied by a change in the degree of oxidation. It is evident that not only the degree of oxidation, but also the way in which the ferrous and ferric iron and oxygen are

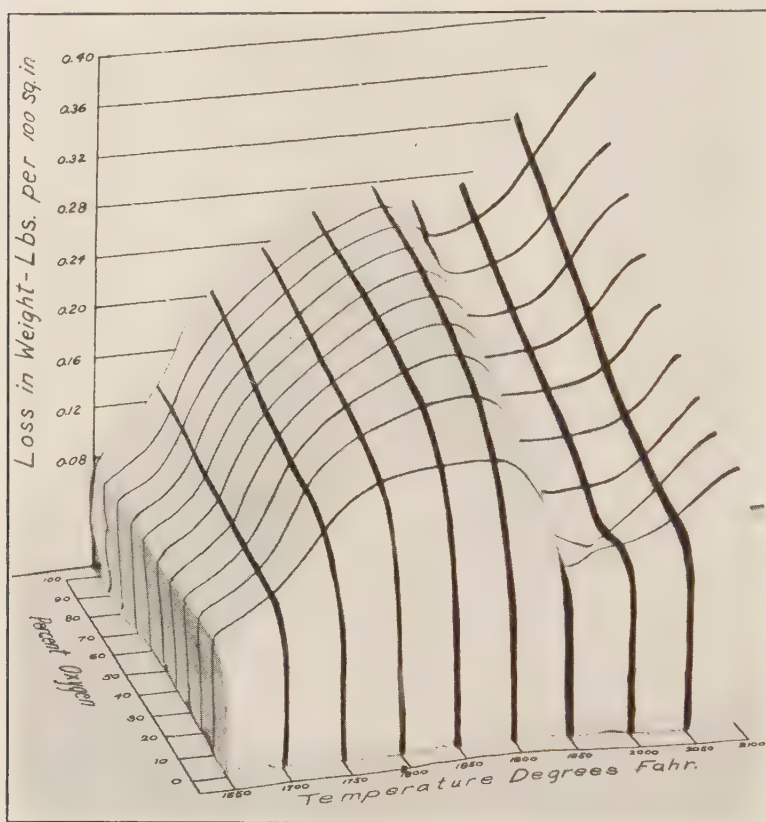


Fig. 9—Three-Dimensional Model Showing the Relationship Between Scaling, Temperature and Oxygen Content.

present in the solid solutions which are possible, must enter into the retarded scaling effects.

By constructing a three dimensional model, a surface can be developed which shows the relationship between the scaling, the temperature, and the oxygen content of the oxidation atmosphere. Such a representation of the data is given in Fig. 9. The time of exposure was one hour in all cases. The reversal in the temperature curves at a constant partial pressure of oxygen is evident from very low oxygen contents to 100 per cent oxygen. The minimum in the curves broadens out at oxygen contents intermediate between air and 100 per cent, occurring over a range of approximately 100 degrees Fahr. at 40 per cent oxygen.

MECHANISM

Before proceeding to the formulation of a possible mechanism to account for the decrease in scaling with increase in temperatures in the range 1850 and 2000 degrees Fahr. (1010 and 1095 degrees Cent.), the conclusions to be drawn directly from the data on effect of temperature, time, and partial pressure of oxygen will be briefly summarized.

A reversal, that is, a decrease in the amount of scaling with increasing temperature, occurs for all oxygen concentrations in the temperature range 1850 to 2000 degrees Fahr. (1010 to 1095 degrees Cent.).

The ferrous iron content of the scales formed undergoes a similar reversal, maxima and minima occurring under approximately the same conditions as for the occurrence of the maxima and minima in scaling.

The reversal or decrease in scaling with increasing temperature occurs for all periods of time up to six hours, the maximum time period used. For a 13 per cent oxygen atmosphere the extent of the reversal was increasing at the end of four hours.

The effect of increasing time on scaling in atmospheres of oxygen, air, and 13 per cent oxygen is in general the same regardless of whether or not the temperature is one at which the scaling is continuously increasing with increase in temperature or one at which the reverse conditions exist. The 100 per cent oxygen atmosphere shows the least retardation in scaling as time increases.

For those concentrations which show the greatest retardation in the rate of scaling with increase in time, the ferrous iron content of the scale is found to decrease. For those concentrations which show a less marked falling off in scaling the ferrous iron content of the scales is found to increase with time.

For certain oxygen concentrations the scaling losses and the ferrous iron content of the scales may remain practically constant over a given temperature range, or retardation of scaling with increasing temperatures may occur without change in the degree of oxidation.

Scaling a Diffusional Process

Upthegrove and Murphy pointed out that the sudden change in the slope of their temperature loss in weight curves for air and oxygen atmospheres was accompanied by the formation of blisters.

They suggested this change in the scaling was the result of a mechanical interruption of the process due to a breaking away of the scale at the blistered areas. This does not appear to adequately account for all of the results observed in the present investigation.

It is quite generally conceded that after the first film of scale is formed the continuation of the oxidation process is a diffusional phenomenon. The general equation for diffusion is

$$\frac{dW}{dt} = -D \frac{dc}{dx}$$

where dW is the amount of the substance under consideration which diffuses through a unit cross section in time dt under a concentration gradient of $\frac{dc}{dx}$, and D is a coefficient. From this it can be seen that the two factors controlling the scaling operation are the concentration gradient or driving force, and the coefficient of diffusion.

The study of the effect of time on scaling offers a means of determining the nature of the concentration gradient. Two types of curves may result in a time-scaling plot. It may be a straight line, that is, one in which the rate of scaling is constant, or a parabolic type, that is, one in which the rate of scaling decreases with time. The constant rate of scaling denotes a cellular membrane in which case the oxidizing gas diffuses mainly through the pores. Under such conditions the concentration gradient or driving force is the difference between the concentration of the oxidizing gas in the scaling atmosphere and at the metal-scale interfaces. The parabolic type indicates that the scale membrane is a continuous type and a continuation of the scaling process occurs by the solution of the oxidizing gas in the scale surface and then a diffusion of this gas inward. In this case the high potential side of the driving force is no longer the concentration of the oxidizing gas in the scaling atmosphere, but is the concentration of the gas in the surface of the scale itself. This will be considered again in the discussion of the diffusion through the various layers formed. The present studies gave time curves of the parabolic type.

As the solubility of the gases in metals generally increases with increasing temperatures, the surface in direct contact with the scaling atmosphere will be capable of taking up more oxygen at higher temperatures. This causes an increase in the concentration gradient or driving force. When differences in the degree of oxidation occur

at different temperatures, the solubility of oxygen may also change and its concentration in the scale may actually decrease when compared with the concentration at a lower temperature.

If it is assumed that the outer layer of the scale in all cases approaches a composition corresponding to Fe_2O_3 , it would appear as if the degree of oxidation of the other layers was of no importance as far as the concentration gradient is concerned, as the overall gradient is governed by the difference in concentration of oxygen

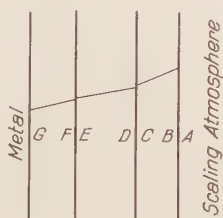


Fig. 10 — Illustrating Degree of Oxidation of Metal Surface.

in the outside surface of the Fe_2O_3 and at the metal scale interface. Due to the layer formation, however, the overall concentration gradient actually consists of several gradients. This is illustrated in Fig. 10. The molecules of the oxidizing gas strike the surface A and are absorbed, building up a definite concentration at B, the maximum concentration possible being saturation. A definite gradient exists from B to C which constitutes the driving force of the outside layer. The oxygen must pass from C to D either by diffusion or reaction. If the nature of the middle layer is such that the solubility of oxygen is lower than in the outside layer, it will not be capable of absorbing the oxygen at D as fast as it reaches C. Therefore the concentration at C will build up, which in turn causes the driving force from B to C to decrease. This reduces the amount of oxygen reaching C. A balance between the amount of oxygen arriving at C and that being absorbed at D is finally reached, when the process settles down to a steady state. Since it has been postulated that the solubility is lower in the middle layer, the concentration gradient for this layer is necessarily small. The manner of transfer of oxygen from E to F is the same as from C to D and another gradient exists from F to G. The concentration at E controls the concentration at F as it would be impossible for the

oxygen to diffuse from E to F if the concentration at F exceeded that at E. In this illustration the middle layer has been made the controlling influence on the driving force, but any of the three layers could be of such a nature so as to control the concentration gradient. Any change in the magnitude of the coefficient of diffusion will affect the scaling losses. There are two factors that affect the coefficient of diffusion; changes in temperature, and changes in the membrane through which diffusion is taking place. An increase in temperature causes an increase in the magnitude of the coefficient, and follows the expression $D \propto T^x$, where D is the diffusivity coefficient, T the temperature and x is an exponent. Changes in the character of the membrane have a definite influence on the magnitude of the diffusivity coefficient. That changes in structure of the scale membrane occur at different temperatures, these changes being confirmed by the chemical analysis of the scale formed, has been previously pointed out. It is evident that the effect of the change in the membrane must be greater than the effect of the increasing temperature on the coefficient of diffusivity to produce the phenomena of the reversal in the temperature scaling curve.

Character of Scale Membrane

A change in the structure of the membrane through which diffusion is taking place, it is thus apparent can materially alter the rate of diffusion through a change in both the concentration gradient and the diffusivity coefficient. It now remains to be shown that the above conditions occur in the scaling of steel. The equilibrium system for iron and oxygen as proposed by Pfeil (9) is given in Fig. 11. In the temperature region studied in this investigation 1650 to 2100 degrees Fahr. (900 to 1150 degrees Cent.) the phases that may be present are $\text{Fe} + \text{FeO}$, FeO , $\text{FeO} + \text{Fe}_3\text{O}_4$, Fe_3O_4 , $\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3$, Fe_2O_3 . From the diagram it is clearly evident that in actual scale formation the phases which are encountered are not the compounds but actually the solid solutions of FeO , Fe_3O_4 and Fe_2O_3 . In fact, without the solid solution formation, concentration gradients would be reduced to zero and continuation of scaling would not be possible but would stop as soon as a film of scale was formed on the metal surface. The extent of the solid solubility at any temperature naturally varies with the different phases. The oxygen content of the scale will then not only vary from a high concentration

at the scale surface to a low concentration at the metal scale interface but also within each of the phases present. The FeO must necessarily be the phase of lowest oxygen content when not dealing with conditions permitting eutectic formation, unless it may be assumed that preferred oxidation may occur, when FeO and Fe will exist together. Since the scale forms in layers, each of these phases which

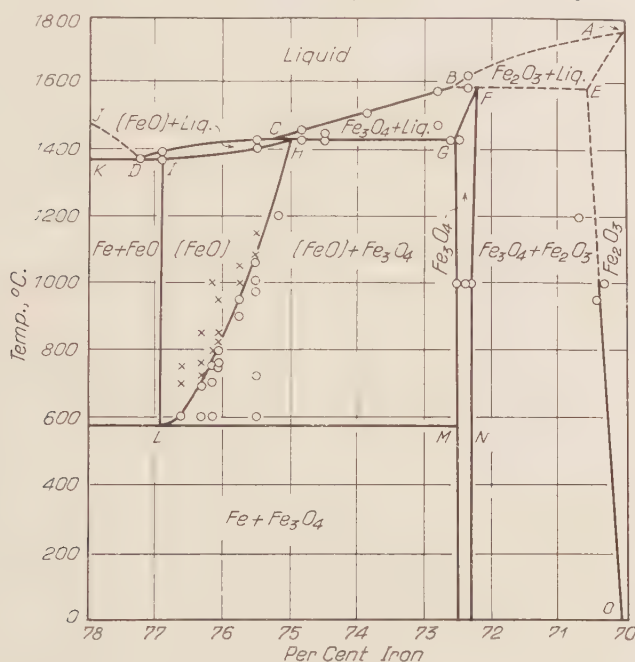


Fig. 11—Equilibrium Diagram of the Iron-Oxygen System from 70 to 78 Per Cent Iron.

are present in any one layer will show a variation in composition, the oxygen-rich concentration always being farthest from the metal scale interface. This difference in chemical composition from one side of the scale layer to the other constitutes the driving force for the diffusional process. A similar gradient exists for the iron concentration, the highest iron content being nearest to the metal scale interface.

Recent work of Jette and Foote on the Fe-O system (Fig. 12) shows the oxygen-rich boundary of the FeO field to reach a maximum at 2010 degrees Fahr. (1100 degrees Cent.). Consideration of their data indicates that this maximum could have been placed nearer

1830 degrees Fahr. (1000 degrees Cent.) without misinterpreting their results. This would point to a maximum solubility for oxygen in FeO solid solution at practically the same temperature as that at which the maximum oxidation loss is observed in the scaling of steel in air, namely 1850 degrees Fahr. (1010 degrees Cent.). The inference that the maximum scaling loss occurs at this temperature

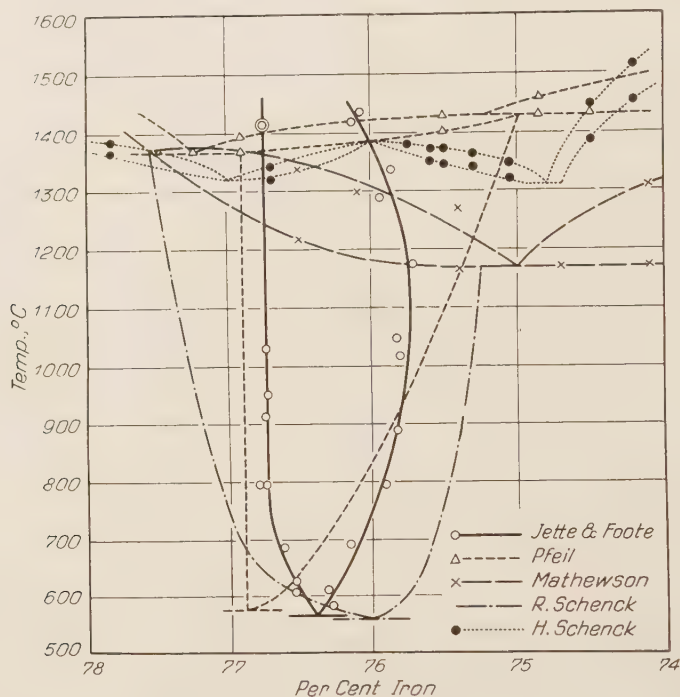


Fig. 12—Wüstite Ranges in the Iron-Oxygen System.

solely because of the maximum solubility should not be drawn as the other factors enter in. At the same time the possibility that the condition of maximum solubility allows for a maximum concentration gradient perhaps should not be ignored.

On the basis that the concentration gradient is directly influenced by the extent of the solid solubility, it follows that the phase having the lowest solubility will exert the greatest influence on the overall rate of diffusion. The amount of this phase present will also be a determining factor as the maximum concentration gradient is set by the limit of solid solubility and increasing the thickness of this phase

of the membrane causes a decrease in the gradient per unit of thickness. The Fe_3O_4 solid solution has the lowest solubility range of all the phases theoretically possible in scale formation within the temperature limits used in this investigation, 1650 to 2100 degrees Fahr. (900 to 1150 degrees Cent.). It would therefore be expected that the scale formed in the temperature regions where a reversal occurs should show a relatively high proportion of Fe_3O_4 solid solution.

The chemical analyses of the scales formed at different temperatures show that the ratios of ferrous to ferric iron have a wide range of values. The ferrous iron content is relatively high at the temperature where a maximum scaling loss is obtained when compared with the ferrous iron content at the temperature where a minimum loss is obtained. At the same time the ferric iron content of the scale formed at the temperature where a maximum is reached is relatively low when compared to the ferric iron content of the scale formed at the temperature where a minimum loss is obtained. The ferric iron content, however, can exist in two of the solid solutions present, Fe_3O_4 and Fe_2O_3 . Considering the Fe_3O_4 as one molecule of Fe_2O_3 and one molecule of FeO , then two thirds of the iron in the Fe_3O_4 is in the trivalent state and one third in the divalent state.

Chemical analysis and micro examinations of the scales formed under the various conditions offer means of determining the character of the scale membrane, that is the nature of the phases and the extent to which they are present. Calculations based on the analysis of the scale and the assumption that the theoretical compounds FeO , Fe_2O_3 and Fe_3O_4 are formed permit the estimation of the maximum amount of the Fe_3O_4 which could be present under any condition. A calculation of this nature which makes no allowance for any ferric iron being present as Fe_2O_3 , but rather assumes all trivalent iron present at Fe_3O_4 , proves a useful aid in the interpretation of the scale photomicrographs. Data from such calculations based on chemical analysis of scale formed in air in four hour runs are given in Table I. The first two columns give the ferrous and ferric iron contents of the scale analysis. In the third column the amount of ferrous iron necessary to combine with all of the ferric iron to form Fe_3O_4 is given. The fourth column shows the difference between the ferrous iron required to form Fe_3O_4 and the divalent iron content of the analysis. A minus sign denotes a deficiency and a plus sign denotes a surplus of divalent iron, that is, the sign indicates whether or not a suf-

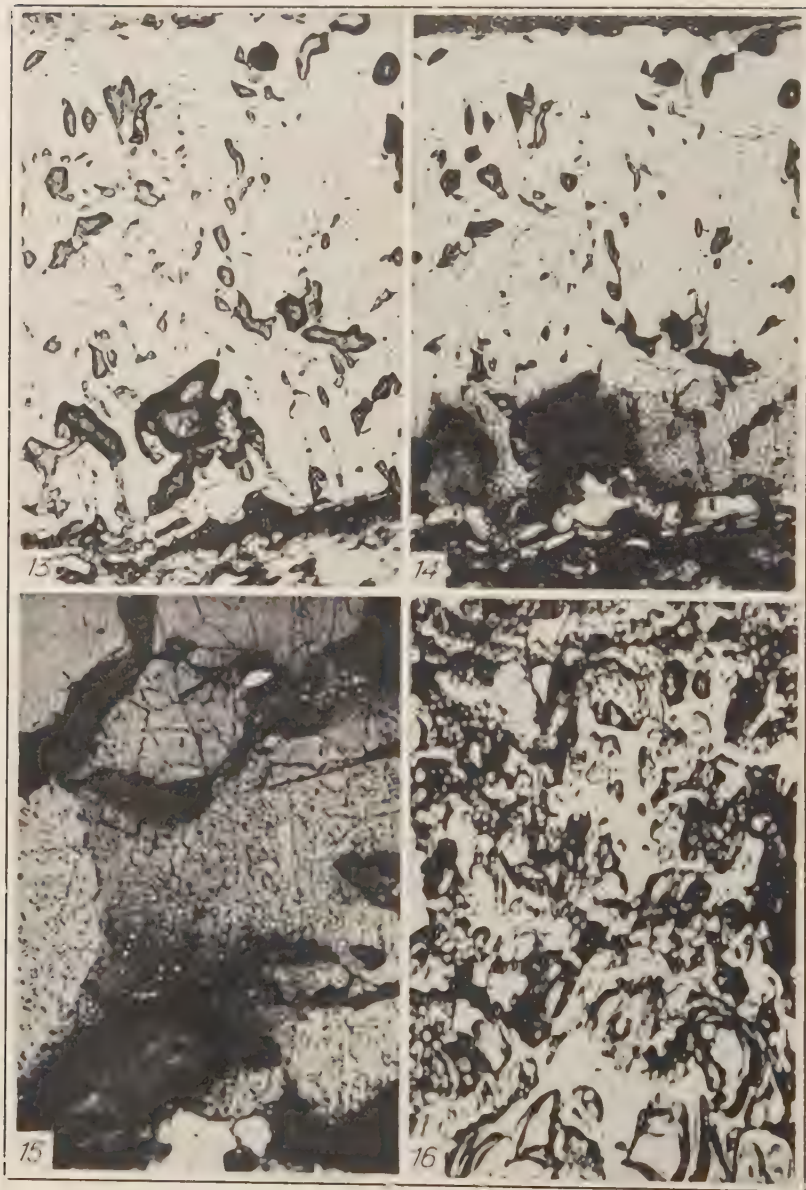


Fig. 13—Scale Formed at 1800 Degrees Fahr. Unetched. $\times 100$.

Fig. 14—Scale Formed at 1800 Degrees Fahr. Etched in 5 Per Cent HCl in Alcohol. $\times 100$.

Fig. 15—Precipitated Phase of the Middle Layer of Fig. 14. $\times 500$.

Fig. 16—Scale Formed at 1915 Degrees Fahr. Etched with 5 Per Cent HCl in Alcohol. $\times 100$.

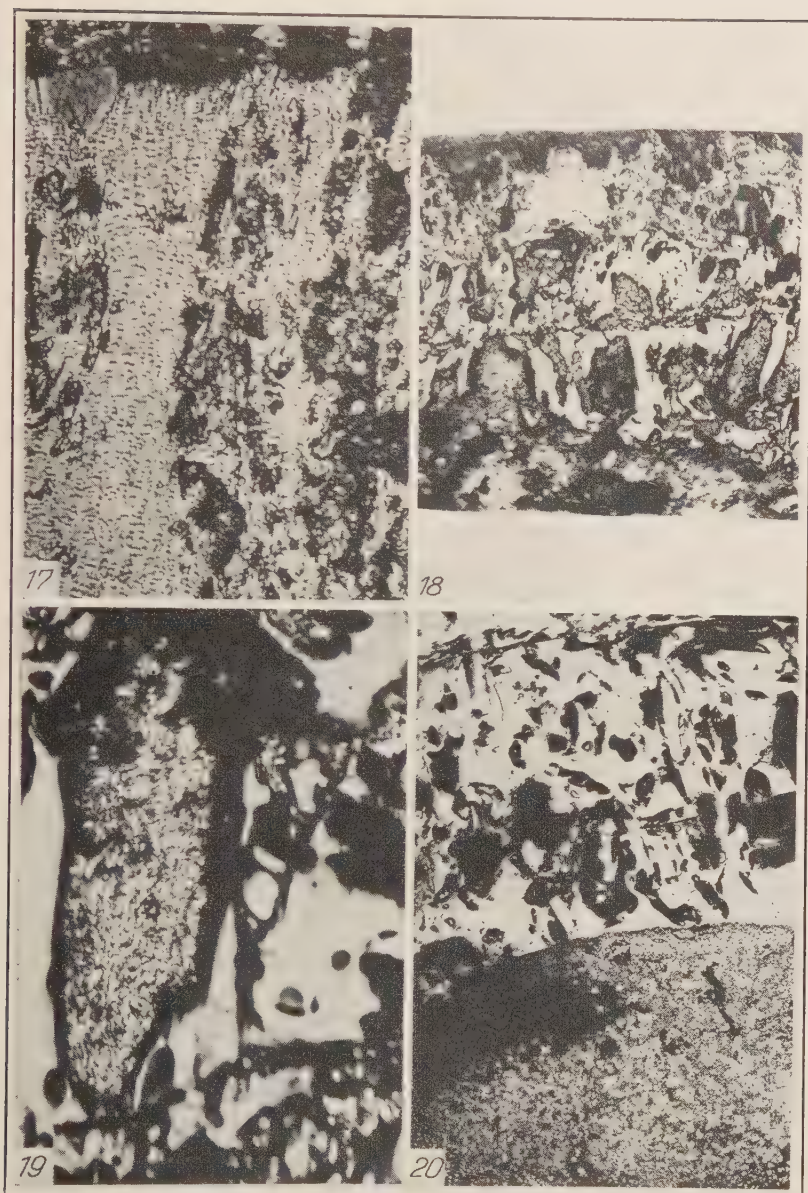


Fig. 17—Inner Layer of Scale Shown in Fig. 16. $\times 500$.

Fig. 18—Scale Formed at 2000 Degrees Fahr. Etched with 5 Per Cent HCl in Alcohol. $\times 100$.

Fig. 19—Columnar Structure of Inner Layer of Fig. 18. $\times 500$.

Fig. 20—Scale Formed at 2100 Degrees Fahr. Etched with 5 Per Cent HCl in Alcohol. $\times 100$.

Table I
Analysis of Scale Formed in Air in 4-Hour Runs

Temp. °F.	Fe ⁺⁺	Fe ⁺⁺⁺	Fe ⁺⁺ for Fe ₃ O ₄	Difference of Fe ⁺⁺ Content
1800	51.80	22.05	11.02	+ 40.78
1915	34.00	39.00	19.50	+ 14.5
2000	21.50	49.40	24.70	- 3.20
2100	31.10	41.60	20.80	+ 10.30

ficient amount of ferrous iron is present in the scale analysis to combine with all of the Fe⁺⁺⁺ to form Fe₃O₄. These particular analyses are given as they correspond to the samples of scale used for the photomicrographs.

Structure of the Scale

The microstructures of the cross section of the scales formed are shown in Figs. 13 through 21. These cross sections are portions of scales which were split off the steel during the quenching operation. Quenching was resorted to in order to retain as far as possible the phase present at the actual temperature of scaling. Great difficulty was encountered in the polishing of the scale due to the brittleness and it was found impossible to entirely prevent some sections from breaking away and leaving voids.

Fig. 13 shows the scale formed at 1800 degrees Fahr. (980 degrees Cent.) in the unetched condition. This same section is shown in the etched condition in Fig. 14. Three layers are evident in Fig. 13, the middle layer comprising approximately 75 per cent of the total cross section; the outside layer being 5 per cent and the inside layer approximately 20 per cent of the area. Upon etching a fine dispersion appears in the middle layer, leaving another narrow layer in relief between the inside and the fine dispersion. This finely divided dispersion is shown at higher magnification in Fig. 15 and corresponds to the decomposed ferrous state postulated by Pfeil. The decomposition of the FeO solid solution results from a decreasing solubility with decreasing temperatures. From the relationship given in Table I it is evident that an excess of FeO will exist at this temperature. Since the specific gravities of FeO, Fe₃O₄ and Fe₂O₃ are so nearly alike, namely 5.28, 5.20, and 5.12 respectively, it follows that the specific volumes of the different oxides are approximately equal; also, the total iron contents of the various solid solutions of FeO, Fe₃O₄, and Fe₂O₃ cannot vary by more than 7.78 per cent if the

theoretical compounds are formed. This difference will actually be less, due to the solid solution formation. Therefore, in order to get a qualitative relationship to establish the identity of the various layers, it may be assumed that the width of a given layer is independent of the type of solid solution present. The evaluation of the

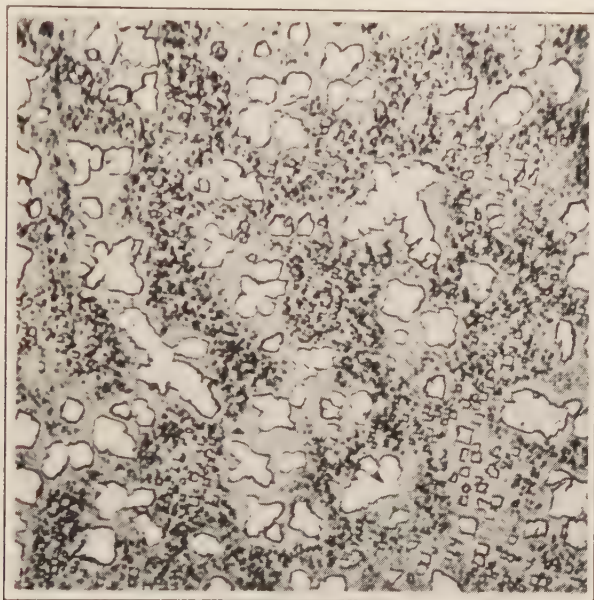


Fig. 21—Inner Layer of Fig. 20. $\times 1000$.

constitution of the various layers may now be undertaken. It has already been pointed out that the middle layer of the scale formed at 1800 degrees Fahr. (980 degrees Cent.) (Fig. 13) comprises approximately 75 per cent of the cross sectional area. From Table I it can be seen that an excess of 40.78 per cent ferrous iron exists which represents 55.5 per cent of the total iron. This immediately establishes the fact that more than one half of the cross section must be the ferrous state. Furthermore, as Jette and Foote have shown that the oxygen-rich solid solution of FeO is composed of Fe_3O_4 dissolved in FeO, an even greater percentage of the cross sectional area must actually be present as the ferrous phase. It therefore follows that the middle layer must be composed of the ferrous phase. If the layer formation is characterized by a progressive change in phases accompanying an increase in the iron content as shown in

Fig. 11, then the outside layer must be a mixture of $\text{FeO} + \text{Fe}_3\text{O}_4$. Examination of this layer at high magnification showed this to be the case. It is, however, entirely possible that minute layers of the other phases out to Fe_2O_3 exist on the outside surface of the scale which were not detected in the present investigation. The inside layer should then be a mixture of $\text{Fe} + \text{FeO}$ solid solution, not in the eutectic mixture as it is formed below the eutectic temperature, but present as a mixture nevertheless.

The formation of a mixture of $\text{Fe} + \text{FeO}$ undoubtedly occurs when the metal surface is undergoing oxidation due to preferential oxidation, but it is difficult to conceive that the oxidation agent will pass this iron in the Fe-FeO mixture on its way to the metal scale interface, without oxidizing it to FeO . Also as the FeO solid solution in the mixture gets richer in oxygen, it will have a decided tendency to dissolve this Fe . Since there is a diffusion of iron taking place, it is possible that the iron of this mixture is taken up by the FeO and the original space occupied by the free iron is not completely filled with oxide, permitting voids to develop. This inside layer (Fig. 13) appears very spongy, suggesting that the above actually does occur. Therefore this layer would be composed of the ferrous phase as is the middle layer (Fig. 13). Two layers composed of the same phase are possible as they have different physical constructions.

Pfeil has demonstrated that the interface of the middle and inner layers represents the original metal surface before oxidation began. This has been confirmed in the present investigation. If the spongy nature of the inner layer is due to the postulations given above, then this offers a possible explanation of why this interface of the inner and middle layers represents the original position of the metal surface before oxidation. Also since the voids do not have a tendency to close, it offers an explanation for this boundary not shifting with continued oxidation. The appearance of the precipitation in the middle layer and the occurrence of the narrow band between the middle and inner layers (Fig. 13) can only be accounted for on the basis of a tempering action. As has been pointed out, the scale split away from the metal on quenching, but did not always become dislodged immediately. Therefore the heat coming out of the steel had to pass partially through this scale while it still was in contact with the steel. This tempering effect could easily cause a precipitation to take place. There is a decreasing solubility with decreasing tem-

perature in the FeO solid solution range. Since the oxygen content of any layer varies from end to end, a critical oxygen content combined with a critical tempering temperature could cause the precipitation to occur at an intermediate place as shown in Fig. 13. This phenomenon was not observed in all cases of scale formed at 1800 degrees Fahr. (980 degrees Cent.).

The scale formed at 1915 degrees Fahr. (1045 degrees Cent.) is shown in Figs. 16 and 17. From Table I it can be seen that there is an excess of ferrous iron over the amount necessary to combine with all of the ferric iron to form Fe_3O_4 . This insures the presence of the ferrous phase. Fig. 16 shows that three layers are present, and an examination of the inside layer at a higher magnification (Fig. 17) shows that this layer is made up of a mixture of the FeO and Fe_3O_4 solid solutions. This then establishes the identity of the middle layer as the Fe_3O_4 solid solution and the outside layer as a mixture of Fe_3O_4 and Fe_2O_3 . When the scaled sample is quenched some scale always adheres to the steel, the splitting away of the oxide always occurring some place in the scale itself. In this case the parting of the scale occurred either at the interface representing the original metal surface, or else in the inner layer shown in the photomicrographs. This is indicated by the fact that no spongy layer exists. At 1915 degrees Fahr. (1045 degrees Cent.) the scaling loss is definitely decreasing with increasing temperature (Fig. 1) and it has also been shown that the Fe_3O_4 solid solution is appearing to an appreciable extent.

The scale formed at 2000 degrees Fahr. (1095 degrees Cent.) is shown in Figs. 18 and 19. Four layers are evident in Fig. 18. The inside layer is spongy and examination at higher magnification shows that it is composed of $\text{FeO} + \text{Fe}_3\text{O}_4$. The next layer following the inside layer is still composed of the $\text{FeO}-\text{Fe}_3\text{O}_4$ mixture but the Fe_3O_4 solid solution is more prominent. The white columnar crystals are Fe_3O_4 and the mottled crystals are a mixture of FeO and Fe_3O_4 . This layer is shown at a higher magnification in Fig. 19. The next layer is the Fe_3O_4 solid solution and the outside layer is comprised of a mixture of Fe_3O_4 and Fe_2O_3 .

The minimum scaling loss in the region of the reversal is attained at the temperature of 2000 degrees Fahr. (1095 degrees Cent.). It has been previously pointed out that at 1915 degrees Fahr. (1045 degrees Cent.) the scaling loss was definitely decreasing and that the Fe_3O_4 solution was appearing in the scale to an appreci-

able extent. It has now been shown that at 2000 degrees Fahr. (1095 degrees Cent.) the Fe_3O_4 content has increased to still greater extent. Furthermore, it may be pointed out that the spongy inside layer is composed of a mixture of $\text{FeO} + \text{Fe}_3\text{O}_4$ which is high in Fe_3O_4 as compared with the inside layer of the scale in Fig. 13. Therefore the retardation in the diffusional process is not only brought about by this spongy mass which breaks up the continuity of the membrane, but also by the fact that the available mass of this material capable of allowing diffusion to take place is high in Fe_3O_4 .

The structure of the scale formed at 2100 degrees Fahr. (1150 degrees Cent.) is shown in Figs. 20 and 21. The inner layer (Fig. 20) is composed of a mixture of $\text{FeO} + \text{Fe}_3\text{O}_4$, which is shown at a higher magnification in Fig. 21. In this case some of the magnetite particles have grown to considerable size. From Table I it can be seen that some excess ferrous phase must exist and it comprises the matrix of the inner layer. The middle layer is Fe_3O_4 solid solution and the outer layer a mixture of Fe_3O_4 and Fe_2O_3 . The Fe_3O_4 content is still relatively high at this temperature (2100 degrees Fahr.) and yet the loss in weight is again increasing with increasing temperatures. This can be accounted for by the fact that the spongy layers which adhered to the metal on quenching, cannot be Fe_3O_4 as it was in the scale formed at 2000 degrees Fahr. (1095 degrees Cent.). This is necessarily true as the inside layer (Fig. 20) is composed of the decomposed ferrous phase and the spongy layer must be composed of either the decomposed ferrous phase or a phase higher in iron content. In addition the solubility range of the Fe_3O_4 solid solution begins to increase in this temperature region as can be seen from Fig. 11. It may also be pointed out that if no increase in the amount of Fe_3O_4 over that formed at 2000 degrees Fahr. (1095 degrees Cent.) occurred, and if the membrane at these two temperatures were identical, the scaling loss at 2100 degrees Fahr. (1150 degrees Cent.) would still be larger due to the increase in the diffusivity coefficient with temperature. The structure of the membrane itself influences the magnitude of the coefficient of diffusivity, but it is impossible to draw any definite conclusions regarding this from the data available at the present time.

SUMMARY AND CONCLUSIONS

The results of this investigation have shown that:

1. A reversal, that is, a decrease in the amount of scaling with increasing temperature occurs from very low oxygen concentrations to 100 per cent oxygen in the temperature range 1850 to 2000 degrees Fahr. (1010-1095 degrees Cent.).

2. The ferrous iron content of the scales formed undergoes a similar reversal, maximum and minimum occurring under approximately the same conditions as for the occurrence of the maximum and minimum for scaling.

3. The reversal occurs for all periods of time up to six hours, the maximum time period used. For a 13 per cent oxygen atmosphere the extent of the reversal was increasing with increasing time at the end of four hours.

4. The effect of increasing time on scaling in atmospheres of oxygen, air, and 13 per cent oxygen is in general the same regardless of whether or not the temperature is one at which the scaling is continuously increasing with increasing temperatures or one at which the reverse conditions exist. The 100 per cent oxygen atmosphere shows the least retardation in scaling as the time increases.

5. For those temperatures which show the greatest retardation in the rate of scaling with increase in time, the ferrous iron content of the scale is found to decrease. For those temperatures which show a less marked falling off in scaling the ferrous iron content of the scales is found to increase with time.

6. For certain oxygen concentrations the scaling losses and the ferrous iron content of the scales may remain practically constant over a given range of temperature, that is, retardation of scaling with increasing temperature may occur without a change in the degree of oxidation.

7. The change in the degree of oxidation causes a change in the membrane structure resulting in an increasing proportion of Fe_3O_4 solid solution in the temperature region where the reversal occurs.

8. The Fe_3O_4 solid solution has the lowest solid solubility range of the phases possible in the scaling system. This solid solubility is a limiting factor governing the concentration gradient or driving potential in the diffusional process. This, in turn, directly influences the rate of diffusion, the lower the driving force the lower the rate of diffusion, all other things being equal.

9. The membrane structure has a direct influence on the magnitude of the diffusivity coefficient. If the changes in the membrane

structure in the region of the reversal are of such a nature that an increase in the diffusivity coefficient results, then the effect of the lower oxygen solubility in the Fe_3O_4 solid solution must be so great that it will overcome the effect of increasing the coefficient of diffusion. On the other hand if the change in membrane structure causes a decrease in the magnitude of the diffusivity coefficient, it will be one of the contributing factors in the reversal in the temperature-loss in weight curve.

10. A theory has been advanced for the occurrence of a reversal in the temperature-loss in weight curves in the temperature region 1800 to 2100 degrees Fahr. (980-1150 degrees Cent.).

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